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## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

## Process for the Hydrogenation of Hydroperoxides

We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Finsbury Circus, London, E.C.2, a British joint-stock Corporation, and KENNETH ALLISON and MAURICE BARRINGTON SPARKE, both of the Company's Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex and both of British nationality, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to a process for the hydrogenation of organic hydroperoxides, particularly to the selective hydrogenation of organic hydroperoxides in the presence of other organic compounds.

According to the present invention there is provided a process for the hydrogenation of organic hydroperoxides which comprises contacting said hydroperoxide in the presence of hydrogen with a platinum group metal catalyst modified by a compound of a metal selected from silver, copper, zinc, cadmium, mercury, tin, lead, arsenic, antimony, bismuth and thallium.

By platinum group metal catalyst throughout the specification is meant the metals themselves or compounds thereof, either unsupported or supported on suitable carrier material, for example, platonic oxide or rhodium supported on charcoal.

The preferred platinum group metal is palladium, particularly palladium supported on a carrier material such as calcium carbonate, barium carbonate, magnesia, barium sulphate, alumina or sepiolite. Particularly suitable modifying compounds for a supported palladium catalyst are compounds of lead, mercury, cadmium and thallium. Non-limiting examples of suitable modified catalysts are mercury, lead, cadmium or thallium-modified palladium supported on calcium carbonate, and lead-modified palladium supported on zinc carbonate, alumina or sepiolite.

Suitably the modified catalysts used in the process of the present invention contain between 0.1% and 500% by weight preferably 100 to 300%, of the modifying compound (calculated as the metal) based on the weight of platinum group metal present in the catalyst.

It has been found that difficulties may be experienced in preparing catalysts capable of providing reproducible results when used for hydrogenating hydroperoxides, and these difficulties may be largely overcome by contacting the platinum group metal catalyst with an aqueous solution of a salt of the modifying metal in the presence of a free mineral or organic acid. In the instance where an organic acid salt of the modifying metal is used, the free organic acid may be the same as or different from that from which the salt is derived. Suitable organic acids are acetic and propionic acids. A suitable mineral acid is nitric acid. The acid should be present in a concentration sufficient to suppress the precipitation of basic salts.

In a further aspect of the present invention, it has been found advantageous to pretreat the modified catalysts with a free-hydrogen-containing gas before use in the hydrogenation process of the present invention. By such a pretreatment, it has been found that the induction period of the subsequent hydrogenation reaction may be substantially reduced and in some cases, eliminated.

The hydroperoxides which may be hydrogenated by the process of the present invention are preferably acyclic and more preferably unsaturated acyclic hydroperoxides. Unsaturated and saturated cyclic hydroperoxides e.g. cyclohexenyl hydroperoxides may be also employed.

One particular application of the invention resides in the selective hydrogenation of organic hydroperoxides, particularly olefin hydroperoxides, in the presence of olefins, for example, methylpentene hydroperoxides in the presence

of methylpentenes. Exemplary of such methylpentene hydroperoxides are those which may be produced, together with other products, by the direct oxidation of methylpentenes. Further, the present process is selective in respect of the hydroperoxide group in a hydroperoxide containing also olefinic unsaturation.

The hydrogenation reaction may be carried out over a wide range of conditions of temperature and pressure. It has been established that ambient temperatures and atmospheric pressure are very suitable, and that no advantages are gained by operation at conditions varying to any great extent from ambient. This is advantageous when unsaturated hydroperoxides are undergoing reaction since at elevated temperatures unwanted thermal degradation products may be formed.

The invention will be more readily understood with reference to the following examples.

#### EXAMPLE 1

A poisoned catalyst was prepared by treating an aqueous suspension of a catalyst containing 10% by weight of palladium on calcium carbonate with an aqueous solution of mercuric acetate, to which has been added 1% of free acetic acid on a water bath. The resulting modified catalyst is hereinafter referred to as catalyst A.

A similar catalyst modified with lead acetate was prepared in an analogous manner to produce a modified catalyst hereinafter referred to as catalyst B.

Table 1 below illustrates details of the catalyst preparation:

TABLE 1

Catalyst	10% Palladium on calcium carbonate weight gms.	Vol. of water ml.	Modifying Solution		Time of heating mins.	Temp. °C.
			Vol. ml.			
A	0.5	6.5	3.5	6.7% wt of mercuric acetate	30	100
B	0.5	10.0	2.0	5.0% wt of lead acetate	22	97

Catalysts A and B were used in a series of experiments in which the selective hydrogenation of tertiary-butyl hydroperoxide in the presence of various olefins was studied. The mixtures used contained 30% by weight of hydroperoxide and the reactions were carried out at ambient temperature and pressure. The results are summarised in the following Table 2 and it can be seen that a very high degree of selectivity is exhibited by the catalysts used.

TABLE 2

Catalyst	Primary Catalyst	Modifying Metal	Olefin	% of hydroperoxide reduced	% of olefin saturated
A	Pd/CaCO <sub>3</sub>	Hg	2-methylpentene-2	98	0.7
B	Pd/CaCO <sub>3</sub>	Pb	2-methylpentene-2	97	0.8
B	Pd/CaCO <sub>3</sub>	Pb	4-methylpentene-2	99	6.1
B	Pd/CaCO <sub>3</sub>	Pb	a mixture containing 53% wt of 2-methylpentene-2 and 43% wt of 2-methylpentene-1.	98	1.1

- The effect of pretreating the catalyst with hydrogen was illustrated by preparing catalyst B as above, and allowing the catalyst to stand in an atmosphere of hydrogen at room temperature and pressure for about 14 hours. This catalyst was then used to selectively hydrogenate tertiary-butyl hydroperoxide in the presence of 2-methylpentene-2 under the conditions indicated above. Without hydrogen pretreatment there was an induction period of 70 minutes before hydrogenation proceeded, but with the pretreated catalyst, the hydrogenation reaction proceeded immediately.

## EXAMPLE 2

- 15 A mercury-modified palladium catalyst was prepared by admixing 0.5 grams of a palladium on calcium carbonate catalyst containing 10% by weight of palladium, 3.0 ml of a 0.7% by weight aqueous solution of mercuric acetate

and 7 ml of water. The mixture was stirred at room temperature for 10 minutes, then at 95–100°C for 30 minutes. The resultant modified catalyst contained 1.4% by weight of mercury.

The modified catalyst was stood in a hydrogen atmosphere overnight and used to hydrogenate a mixture containing 28.8% by weight of tertiary butyl hydroperoxide and 71.2% by weight of a methylpentene mixture containing 95% 2-methylpentene-2.

The reaction was carried out at ambient temperature and pressure using 1 part of the mixture and 0.05 parts of the modified catalyst. Methanol was also added to the reaction medium as a solvent.

The results achieved are tabulated below in Table 3 and include a comparison with the same palladium catalyst but which was unmodified. The results show the selectivity of the modified catalyst to the hydroperoxide.

TABLE 3

Catalyst	% hydroperoxide reduced	% Methylpentene reduced
Modified	97	0.8
Unmodified	75	19.9

## EXAMPLE 3

- 45 A lead-modified catalyst was prepared by admixing 0.495 grams of a palladium on alumina catalyst containing 10% by weight of palladium, 0.22 mls of water and 0.2 grams of a solution prepared by dissolving 2.78 grams of lead acetate in 20 N/20 acetic acid. The slurry was shaken at room temperature for 30 minutes and 1 ml of concentrated ammonia was added. The modified catalyst was filtered, washed and dried then pretreated with hydrogen by being left standing in a hydrogen atmosphere over night.

- 50 This catalyst was used to hydrogenate a methylpentene oxidate containing 18.3% by weight methylpentene hydroperoxide and

72.9% by weight methylpentenes. The methylpentene mixture contained 53% by weight 4-methylpentene-2, 39.7% by weight 2-methylpentene-2 and 7.3% by weight other hexenes.

The hydrogenation was carried out at ambient temperatures and pressure using 0.1 part of the modified catalyst and 2.01 parts of the oxidate.

The results achieved are set out in Table 4 and include a comparison with the unmodified catalyst. Again it is to be noted that the modified catalyst shows much greater selectivity for the hydroperoxide than for the olefin, the degree of hydrogenation of the olefin being reduced by 50%.

TABLE 4

Catalyst	% Hydroperoxide reduced	% Methylpentene reduced
Modified	97.5	0.8
Unmodified	97.1	1.6

- 75 In the above experiment it was shown that the products of hydrogenation of the hydroperoxides with the modified catalyst were the corresponding unsaturated alcohols, thereby

illustrating that the modified catalyst is selective for the hydroperoxy group.

#### EXAMPLE 4

5 A lead-modified catalyst was prepared by admixing 0.5 grams of a palladium on calcium carbonate catalyst containing 10% by weight of palladium, 6 mls of water and 4.1 mls of an aqueous lead acetate solution containing 5% by weight of lead acetate and 1% by weight of glacial acetic acid. The suspension was stirred at room temperature for 10 minutes

and then at 100°C for 30 minutes. The catalyst was filtered, washed and dried, then pre-treated by standing it in a hydrogen atmosphere overnight. The modified catalyst contained 20.9% by weight of lead.

The catalyst was used to hydrogenate a range of hydroperoxide/olefin mixtures and the results achieved are set out in Table 5.

The hydrogenation was carried out at ambient temperature and pressure using 0.05 parts of the modified catalyst, 1 part of the mixture and methanol as a solvent.

TABLE 5

Mixture		% ROOH reduced	% Olefin reduced
ROOH % wt.	Olefin % wt.		
TBHP 21.5	78.5 { 4MP2 98.6 other hexenes 1.4	99.8	0.8
TBHP 20.4	79.6 { 2MP1 91.7 other hexenes 8.3	99.8	0.4
TBHP 33.8	66.2 { 2MP2 93.5 other hexenes 6.5	98.0	0.4
MPROOH 8.8	90 { 2MP1 31.2 2MP2 63.5 other hexenes 5.3	97.0	0.2

ROOH = hydroperoxides  
TBHP = tert. butyl hydroperoxide  
MPROOH = methylpentene hydroperoxides  
4 MP2 = 4-methylpentene-2  
2 MP1 = 2-methylpentene-1  
2 MP2 = 2-methylpentene-2

#### WHAT WE CLAIM IS:—

1. A process for the hydrogenation of organic hydroperoxides which comprises contacting the hydroperoxide in the presence of hydrogen with a platinum group metal catalyst modified by a compound of a metal selected from silver, copper, zinc, cadmium, mercury, tin, lead, arsenic, antimony, bismuth and thallium.

2. A process as claimed in claim 1 wherein the platinum group metal is palladium.

3. A process as claimed in claim 1 or 2 wherein the modified catalyst contains between 0.1 and 500% by weight of the modifying component (calculated as the metal) based on the weight of platinum group metal.

4. A process as claimed in any one of the preceding claims wherein the modified catalyst is pre-treated with hydrogen before use.

5. A process as claimed in any one of the preceding claims wherein the organic hydroperoxide is an olefin hydroperoxide.

6. A process as claimed in claim 5 wherein the hydroperoxide is a methylpentene hydroperoxide.

7. A process as claimed in any one of the preceding claims wherein the hydroperoxide is selectively hydrogenated in the presence of olefins.

8. A process as claimed in claim 7 wherein the hydroperoxide is selectively hydrogenated in the presence of at least one methylpentene.

9. A process as claimed in any one of the preceding claims wherein the hydrogenation is effected at ambient temperatures and atmospheric pressure.

10. A process as claimed in claim 1 substantially as described with reference to the Examples.

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